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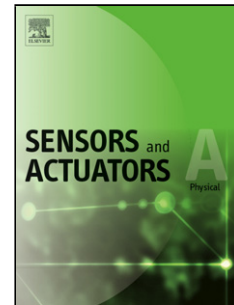
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1 Wheat gluten, a bio-polymer layer to monitor relative 2 humidity in food packaging: electric and dielectric 3 characterization

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12 **Abstract:** Thin wheat gluten protein film, largely investigated as eco-friendly material for
13 food packaging, is investigated as a relative humidity monitoring polymer deposited on
14 designed and manufactured interdigital capacitor (IDC) systems, on the frequency range from
15 30 MHz to 1000 MHz. The ability of wheat gluten to interact with water molecules was
16 characterized and assessed in terms of electrical and dielectric properties with the IDC
17 technique. When relative humidity increases from 20% to 95% RH at 25°C, the dielectric
18 permittivity and loss change from 5.01 ± 0.04 to 9.79 ± 0.06 and from 0.39 ± 0.01 to 1.48 ± 0.02
19 respectively. The dielectric permittivity and loss are very sensitive to relative humidity and
20 increase exponentially due to the comparable exponential increase of wheat gluten water
21 content versus relative humidity. The accessibility of water molecules and the plasticization of

22 wheat gluten results in an increase in the water absorbed by the protein from 3.6% (at 20%
23 relative humidity) reaching up to 33.6% (at 95% relative humidity) of the dry weight. The
24 dependence of both dielectric permittivity and dielectric loss of wheat gluten on relative
25 humidity offered the possibility to use the protein for monitoring relative humidity in packed
26 food products. For this purpose, wheat gluten is foreseen to be coupled with Ultra High
27 Frequency (UHF) Radio Frequency Identification (RFID) systems, giving a cost-effective, low-
28 energy consuming and reliable solution for traceability and monitoring of food packed products.

29

30 **Highlights**

- 31 • Novel study based on wheat gluten development as relative humidity sensor.
- 32 • High coupling potential of wheat gluten with Ultra High Frequency Radio Frequency
33 Identification systems.
- 34 • Retro-simulation for the determination of dielectric permittivity and loss.
- 35 • Exponential increase in dielectric permittivity and dielectric loss in controlled relative
36 humidity conditions.
- 37 • Interaction of water molecules with wheat gluten network.
- 38 • Determination of the sensitivity of wheat gluten as a function of relative humidity.

39 **Keywords:** Dielectric properties, wheat gluten proteins, relative humidity monitoring, RFID.

40

41 1 Introduction

42 Modification of relative humidity in food products is highly impacting food quality and safety
43 by inducing for example irreversible alteration of their texture, spoilage and/or pathogens
44 microbial growth during storage. Due to the consumer's demand for high quality food products,
45 many efforts are devoted to monitor and control the variation of relative humidity in food
46 packages and in packed food products, giving precious information about the evolution of food
47 quality in packages.

48 To reach this objective, a protein has been chosen as part of this work to mimic the behavior of
49 food products and the evolution of relative humidity in packages. Wheat gluten being itself a
50 wheat protein, usually found in dry food products such as cereals, bread or biscuits, has a
51 hydrophilic behavior and is very sensitive to relative humidity. It has been broadly studied at
52 high relative humidity for its gas properties [1] and increasingly investigated for its unique mass
53 transfer properties [2–5]. The high permeability of wheat gluten to carbon dioxide and (to a
54 lower extent) oxygen resulted in a high permselectivity (ratio of carbon dioxide permeability to
55 oxygen permeability) of the material [1], making them interesting for packaging applications,
56 such as fresh fruit and vegetable packages [5–7].

57 The complex combination of bonds (electrostatic interactions, van der Waals forces, salt
58 bonding, hydrogen bonding and disulfide bonding) [8–11] in the wheat gluten network
59 contribute to the stabilization of the protein structure and provide strong dipole-dipole
60 interactions, sharing of electron pairs between atoms (stable electronic configuration) and
61 electrical interaction of low intensity between atoms and molecules [12–15]. Wheat gluten is
62 thus considered as a polarizable material, having dielectric properties (permittivity and
63 dielectric loss). Most of the work carried on wheat gluten was performed on its gas transfer
64 properties as aforementioned and on the electrical behavior of wheat gluten dough or powder

65 at 200 MHz, 915 MHz, 2000 MHz, 10000 MHz, 16000 MHz and at 20000 MHz [8,16–18], but
66 has never been studied as a potential film-based material for relative humidity monitoring,
67 relied on its dielectric property variations at 868 MHz.

68 The originality of the present study resides in the study of wheat gluten proteins for relative
69 humidity monitoring, at 868 MHz, in the perspective to be used with UHF RFID tags having
70 the aforementioned working frequency. Furthermore, wheat gluten (being a wheat protein)
71 mimics mechanisms induced in food products when exposed to relative humidity giving
72 therefore a close measurement of the state of food. Wheat gluten is probably one of the best
73 candidates for the monitoring of relative humidity in packed food products. Interdigital
74 capacitors (IDC), being widely used in chemical, humidity and biological sensing, as well as
75 for electrical and dielectric characterization of materials [19], have been used for electrically
76 characterizing wheat gluten, coated on the comb-like electrodes. The dielectric permittivity and
77 dielectric loss of wheat gluten have been determined by retro-simulation at the working
78 frequency of UHF passive RFID tags (868 MHz), for a foreseen coupling of both in an optimal
79 way. The impact of relative humidity on the dielectric properties of wheat gluten, as well as on
80 its sensitivity and hysteresis have been analyzed and discussed.

81 2 Materials and Methods

82 2.1 Interdigital capacitor (IDC) sample

83 The design of the IDC system was performed using ANSOFT® software, which is a high
84 performance electromagnetic simulation software. The IDC system design technique was
85 already developed in a previous study [20]. In order to have an IDC system (figure 1 (a)) having
86 the desired frequency range (up to 1000 MHz), the following geometrical dimensions were
87 used: $W_2=0.4$ mm, $E_2=0.4$ mm, $L_2=10$ mm, $C_2=2$ mm, $I_2=1$ mm, $J_2=7.4$ mm, $G_2=12.4$ mm,
88 number of fingers (N)=8 and with a substrate (FR4) dielectric permittivity of 4.8.

89 The designed IDC systems were manufactured by CIRLY, France (figure 1 (b)), in order to
90 have homogeneity on all samples. The IDC system electrodes are made of copper metal
91 deposited on a prefabricated circuit board made of a composite of glass fiber reinforced epoxy
92 resin (thickness 1.6 mm). The thickness of the electrode fingers (17 μm) being fixed by the
93 manufacturer, were also kept fixed in the design process.

94

95 Figure 1: Designed interdigital capacitor (a), manufactured interdigital capacitor system
96 casted with wheat gluten having a capacitive behavior up to 1000 MHz (b).

97

98 2.2 Wheat gluten sample

99 2.2.1 Solution preparation

100 Wheat gluten (amygluten 110) powder (7.2 wt % of moisture and 76.5 wt % of protein, 14.2%,
101 8.1% and 1.2% dry weight of carbohydrates, lipids and ashes respectively) was provided by
102 Amylum (Mesnil St Nicaise, France). Sodium sulfite and acetic acid were obtained from Sigma-
103 Aldrich (St Quentin, France). The wheat gluten solution was prepared at room temperature
104 (25°C) and humidity (50% RH). 30 g of wheat gluten powder was dispersed under shaking in
105 50 ml of a sodium sulphite solution (0.06 g sodium sulphite for 50 ml of distilled water) to
106 reduce disulfide bonds in the wheat gluten protein. The mixture was left to settle for 30 minutes.
107 The pH of the solution was adjusted to 4 by adding 3.4 ml of 50/50 v/v solution of acetic acid.
108 The mixture was stirred. The solution was finally adjusted to 130 ml by adding deionised water
109 and mixed. The prepared wheat gluten solution was left degassing under vacuum for one night
110 [21,22] and used within one week.

111 2.2.2 Sample preparation – Solvent Casting method

112 **Sample preparation:** 1 ml of wheat gluten solution was cast onto IDC systems using an E409
113 blade coater from Erichsen (France), in order to cover the whole comb-like structure. The coater
114 was equipped with the **number 4** blade having spires of 0.51 mm, in order to create a humid
115 film deposit having a thickness of 40 μm . The speed was set to **1 mm/s**. The sample was left to
116 dry for 24 hours at room temperature and at 50% of relative humidity.

117 **Self supported wheat gluten:** The wheat gluten solution was cast onto glass panes and left to
118 dry under a constant flow of air, at room temperature and 50% of relative humidity. After
119 drying, circular samples were cut from the wheat gluten layer.

120 **Thickness measurement of wheat gluten layer:** The average thickness of the layer deposited
121 onto IDC systems and glass panes was measured at room temperature and humidity with a
122 profilometer. 5 measurements were performed at 10 random positions. The thickness of the
123 wheat gluten layer is equal to $9.37 \pm 1.10 \mu\text{m}$.

124 2.2.3 Structural characterization

125 **Dynamic Vapor Sorption (DVS):** Water vapor sorption measurements were carried out at
126 25°C over a wide range of relative humidity from 0% to 95%, making use of a microbalance
127 apparatus (Surface Measurement System Ltd, London, UK). **The relative humidity range on**
128 **which the experiment was conducted was made possible due to the precision of the apparatus**
129 **(microbalance) used. Relative humidity was controlled in a hermetically closed chamber.** The
130 process is described in another publication [23]. The self supported wheat gluten layers were
131 used and left for equilibrium at 0% RH in a dessicator for 72 hours. They were then inserted
132 into the microbalance and left for equilibrium at 0% RH for 12 hours to establish a dry mass.
133 The layers were then exposed to different relative humidity values by a continuous air flow
134 having a specific relative humidity value. The different relative humidity values were

135 programmed in the software controlling the microbalance. Mass equilibrium was reached at
136 each relative humidity level by measuring the mass change over time, $dm/dt < 0.002\text{ mg/min}$,
137 of wheat gluten or by imposing a time frame for each relative humidity step. Once equilibrium
138 was achieved, the apparatus shifted to the next programmed RH stage, and so forth. Sorption
139 and desorption cycles were performed to determine the reversibility of the wheat gluten
140 material. The sorption and desorption isotherms were built, as well as the sorption and
141 desorption kinetic curve. The experiment was performed as triplicates.

142 2.3 Electrical measurements

143 2.3.1 Measurement of the impedance (real and imaginary parts) with interdigital 144 capacitor systems

145 Impedance measurements were performed using a vector network analyzer (VNA) (Hewlett-
146 Packard 8753D) with an open-ended coaxial cable fitted with a coaxial connector (SMA
147 connector), calibrated prior to connection with IDC systems, using three different types of
148 loads: open circuit, short circuit and a $50\ \Omega$ load, over a frequency range up to 1000 MHz.

149 The coaxial cable was fixed to the extent possible in order to avoid stray capacitors due to cable
150 movements after calibration and connected to IDC system located in a chamber where relative
151 humidity and gases were controlled. Relative humidity was increased from 20% to 95% ($\pm 1\%$)
152 using a two-pressure process. The equipment consists of two chambers maintained at the same
153 temperature. In the saturator chamber, air is saturated with water vapor at high pressure. The
154 air then passes through to the test chamber (containing the IDC system), which is at a lower
155 pressure, thus reducing the air pressure, and consequently its relative humidity with a precision
156 of ± 1 at 95% RH. **Relative humidity value extremities such as 0% RH and 100% RH being non-**
157 **stable were avoided due to experimental and material limitations.**

158 The impedance real and imaginary component, as well as frequency were acquired at fixed time
 159 intervals and saved by a program developed on Labview software using a host computer. The
 160 IDC system is represented by an equivalent resistance-capacitance (RC) circuit used in other
 161 studies [24,25]. The associated real and imaginary parts are represented by equation 1 and
 162 **equation 2** respectively, where both are frequency dependent.

$$Z_r = \frac{R}{1 + (RC\omega)^2} \quad \text{Equation 1}$$

$$Z_{img} = -\frac{R^2 C \omega}{1 + (RC\omega)^2} \quad \text{Equation 2}$$

163 where R represents the resistance, C the capacitance and ω the angular frequency.

164 Electrical measurements were performed in triplicate using the IDC systems in air, coated with
 165 wheat gluten, at 433 MHz, 868 MHz and 960 MHz after stabilization was reached.

166 2.3.2 Identification of dielectric permittivity and loss of wheat gluten by retro- 167 simulation of IDC systems

168 The identification of the dielectric properties of wheat gluten was performed by simulation with
 169 ANSOFT® software using geometrical and substrate (FR4) parameters of the designed IDC
 170 system. The **identification** procedure was developed in a previous study [20] **where the**
 171 **permittivity and dielectric loss were obtained by comparing the simulated impedance values to**
 172 **the measured values at the specified frequency.** The only modification performed to the IDC
 173 system was the addition of the wheat gluten layer on top. This layer represented the dielectric
 174 whose permittivity and loss were varied and re-injected in the simulation procedure. By
 175 comparing the simulated impedance values to the measured ones at the specified frequency and
 176 upon matching, the dielectric permittivity and loss of the wheat gluten layer were obtained.

177 3 Results and discussion

178 3.1 Dynamic Vapor Sorption measurements

179 3.1.1 Moisture sorption kinetics

180 As wheat gluten is known to be very sensitive to humidity, dynamic vapor sorption
181 measurements were performed, at 25°C, on a wide range of humidity values (from 0% to 95%
182 of relative humidity). The necessary time for wheat gluten to be in equilibrium with the
183 surrounding atmosphere was determined using water vapor sorption isotherms plots of the self-
184 supported wheat gluten layers. The water content on a dry basis (d.b) was calculated using
185 equation 3.

$$\text{Water content (\%)} = \left(\frac{M_w - M_d}{M_d} \right) \times 100\% \quad \text{Equation 3}$$

186 where M_w is the mass of the wet wheat gluten sample at equilibrium and M_d the dry mass of
187 the wheat gluten sample.

188 The results are presented in figure 2, giving the stabilization time for the capacitance value and
189 the mass intake for each humidity step when a sorption and desorption process was performed.
190 For each humidity value, when a change in mass with respect to time (dm/dt) was recorded and
191 remained constant, the experiment proceeded to the next programmed humidity stage. In the
192 present study, this information is important to know the necessary conditioning time of wheat
193 gluten at each humidity level and the stabilized electrical measurement (capacitance).
194 Fundamentally speaking, at low relative humidity (0% to 50% RH), the net change in mass was
195 up to 8.03% d.b and the capacitance value increased from 6.46 pF to 6.53 pF. In this state, few
196 bind water molecules are present in the wheat gluten network, where a short delay is necessary
197 for equilibrium (~1 hour). At medium relative humidity (50%-70% RH), the net mass increased

198 from 8.03% to 10.2% d.b and the capacitance from 6.53 pF to 6.72 pF. In that phase, the water
199 content of the wheat gluten layer is still low but present under the form of a monolayer (at
200 25°C). Within this monolayer, water molecules present are directly linked with hydrophilic
201 groups. A delay of approximately 4h30 is necessary for the monolayer formation and
202 equilibrium. With increase in relative humidity, the amount of water content increases, forming
203 clusters with the present monolayer. This linking takes place around 70%-90% of relative
204 humidity increasing consequently the net mass from 10.2% to 23.09% d.b, the capacitance from
205 6.72 pF to 7.66 pF and the necessary time for equilibrium is approximately 5 hours. Another
206 phenomenon occurs at even higher relative humidity (90%-95% RH), with the settling of free
207 water in the wheat gluten network with an increase in the net mass from 23.09% to 33.6% and
208 the capacitance from 7.66 pF to 8.47 pF, but a longer delay is required for equilibrium (~8h30).
209 In spite of this, the protein is one of the best candidates for monitoring food quality change
210 within packages because:

- 211 i) As it was specified, wheat gluten mimics the behavior of food products and would
212 give a close measure of what is actually taking place within the food material.
213 Moreover, the stabilization of the capacitance value at each relative humidity level
214 is promising to electrically monitor the packed food products.
- 215 ii) Foreseen food packages containing fresh food (~95% RH) have a shelf life of
216 approximately 1 week, which is much more than the required equilibrium time. It
217 can thus be concluded that wheat gluten would give an accurate measurement of
218 relative humidity within the packed food product.

219

220

221 Figure 2 : Net change in mass (+) and capacitance (▲) of wheat gluten layer as a function of
222 relative humidity (—) and time.

223

224 3.1.2 Sorption and desorption isotherms

225 The sorption and desorption isotherms of wheat gluten are represented in figure 3 which clearly
226 highlights the hydrophilicity of wheat gluten. The results are in the range of those reported by
227 several authors for wheat gluten and zein films [18,26]. The water sorption and desorption
228 isotherms displayed a sigmoid evolution on the complete studied relative humidity range, which
229 is specific to hydrophilic materials, and is also reported by both authors. In addition, sorption
230 isotherms of food materials generally have a sigmoid shape and are useful for the determination
231 of the shelf life and to access background operation such as drying, conditioning, mixing,
232 packaging and storage [27]. Wheat gluten isotherm curve, having precisely the same shape,
233 indicates its close behavior to food materials. The sorption isotherm curve also gives
234 information about the specific interaction between water molecules and the products since it
235 directly relates the thermodynamic potential of water on the system to its mass fraction. If it is
236 considered that hydration of wheat gluten occurs by successive layers, the isotherm curve in
237 figure 3 can be divided into several regions related to a decrease in the intensity of interactions
238 among proteins in the wheat gluten matrix:

- 239 i) RH 0% - 50% corresponds to few bind water molecules with strong hydrogen and
240 hydrophobic bonds among wheat gluten proteins (strong protein-protein
241 interactions).
- 242 ii) RH 50% - 70% coincides with increasingly bind water molecules with the wheat
243 gluten network to high energy sorption sites (monolayer formation).

244 iii) RH 70% - 90% corresponds to successive adsorption of monolayers (water molecule
245 monolayers) interacting mainly by hydrogen bonds. It can also be seen at this stage
246 as cluster formation with increasing movement of the molecular chain.

247 iv) RH 90% - 95% is related to the presence of free water within the wheat gluten
248 network due to their accumulation by capillary. In this region, interactions among
249 proteins of the wheat gluten network are very weak at the expense of interactions
250 with and between water molecules themselves.

251

252 Figure 3: Absorption and desorption isotherms of wheat gluten conditioned at different
253 relative humidity values.

254

255 3.2 Swelling of wheat gluten layer

256 The ability of a material to swell is a property of polymers induced by their macromolecular
257 structure, caused by the sorption of liquids or vapors from the surrounding environment. Fruits
258 and vegetables are known to swell or lose water the same way as wheat gluten. A 90% to 95%
259 relative humidity atmosphere is needed for the proper conservation of fruits and vegetables and
260 to prevent shrinking of the materials. On the other hand, a low relative humidity environment
261 around food produce causes their shriveling and causes crack formation resulting in
262 aesthetically displeasing products. According to authors who worked on wheat gluten coated
263 on paper substrate, micro-fractures on the material surface were revealed at low relative
264 humidity and were reduced as relative humidity increased [28]. At 60% RH some of the cracks
265 disappeared completely. It can be assumed that at 95% RH, a defect-free surface was obtained.
266 The disappearance of the fractures is due to the swelling of the wheat gluten layer. It should be
267 made clear that the fractures do not completely penetrate the layer down to the electrodes or the
268 substrate. At high relative humidity, the swelling of the layer increases its integrity (continuous

269 layer at the surface). It can also be considered that at high humidity, bigger cracks are filled
270 with water (free water) due to capillarity.

271 3.3 Wheat gluten electrical performances

272 3.3.1 Physical characterization

273 Prior to coating of wheat gluten on IDC systems, the verification of the physical parameters of
274 the manufactured IDC systems was performed using a profilometer. There was a good
275 agreement between the measured physical parameters and the design parameters. Furthermore,
276 the measured electrical properties of the uncoated IDC systems were close to the simulated
277 electrical properties (table 1) indicating their correct manufacture. These measurements were
278 performed at 25°C and at 20% of relative humidity.

279

280 Table 1: Comparison of experimental and simulated electrical properties of uncoated IDC
281 systems.

282

283 3.3.2 Impedance measurements

284 Impedance measurements were performed between 20% and 95% of relative humidity, where
285 each humidity step was maintained constant until the impedance reached a steady state value.
286 The impedance real component is represented in figure 4 (a) and the impedance imaginary part
287 in figure 4 (b). As illustrated in figure 4 (a), the real part increases from $0.15 \pm 0.05 \Omega$ to
288 $2.06 \pm 0.21 \Omega$ when relative humidity increases from 20% to 95% at 868 MHz, with a sharp rise
289 noted as from 70% of relative humidity. The impedance imaginary component (figure 4 (b))
290 has negative values, confirming the capacitive behavior of the IDC system. The imaginary
291 component increases from $-29.12 \pm 0.36 \Omega$ to $-21.28 \pm 0.61 \Omega$ for the same conditions as for the
292 real component that is, 20% to 95% of relative humidity at 868 MHz. Similarly, the rise
293 becomes significant as from 70% of relative humidity, due to the increasing water content in

294 the wheat gluten film. It is also clear that the sensitivity of wheat gluten is very low at low
295 relative humidity values and that the sensitivity becomes significant as from 70% RH. This is
296 convenient for the foreseen applications with fresh food products where relative humidity
297 within the packaging is estimated to be at approximately 95% RH. Moreover, if dry foods such
298 as cereals are monitored, an alarm for threshold relative humidity value overrun can be
299 programmed. In that case, if the package is accidentally opened, integrity is lost resulting in an
300 increase in the headspace relative humidity, activating the alarm. Wheat gluten is therefore a
301 good candidate for these types of applications.

302 In order to have a better illustration of the increase in electrical properties, the relative variation
303 of the impedance imaginary part is shown on figure 5 at different frequencies (433 MHz,
304 868 MHz and 960 MHz) and as a function of relative humidity. **It has to be specified that 433**
305 **MHz, 868 MHz and 960 MHz are frequency values corresponding to RFID systems working at**
306 **these different frequency values.** As it can be observed, the impedance increases drastically
307 with relative humidity. Comparing the impedance values at each humidity step, one can observe
308 the small change in the impedance value from 20% to 50% of relative humidity for 960 MHz
309 and 868 MHz. A slightly greater change is recorded for 433 MHz. But for higher relative
310 humidity values, the change in impedance is different for 433 MHz than the other two
311 frequencies (868 MHz and 960 MHz), particularly at 95% of relative humidity where the delta
312 change is twice for 433 MHz than at 868/960 MHz. This is because more elements (interface,
313 dipoles and charges) are under the influence of the electromagnetic field at low frequency. As
314 such, at high relative humidity, the effect of water on those elements is more pronounced,
315 increasing the significance of the change in the electrical properties due to water molecules.
316 One can thus find the lower frequency range very attractive for developing the material.

317 However, in the present study, the target RFID system is 868 MHz based justifying the pursuit
318 of this study at 868 MHz.

319

320 Figure 4: Impedance real (a) and imaginary (b) component as a function of frequency from
321 20% to 95% of relative humidity (RH), at 25°C.

322

323

324 Figure 5: Relative variation of the impedance imaginary component with increase in relative
325 humidity, at 433 MHz, 868 MHz and 960 MHz.

326

327 3.3.3 Identification of dielectric parameters

328 The identification of the dielectric loss at a frequency of 868 MHz (figure 6 (a)) was performed

329 by FEM (finite element method) simulation, using the impedance real component, which

330 represents the energy loss in the wheat gluten layer. The dielectric permittivity was also

331 simulated at 868 MHz (figure 6 (b)) using the impedance imaginary component. Both

332 simulations were performed for increasing and decreasing relative humidity values at 25°C to

333 further evaluate the hysteresis. The dielectric loss increases exponentially from 0.39 ± 0.01 to

334 1.48 ± 0.02 and back to 0.401 ± 0.006 . As it can also be noticed, the increase in dielectric loss

335 becomes more significant starting from 70% of relative humidity in the same way as the

336 impedance real part. Regarding the dielectric permittivity, an exponential increase is illustrated

337 from 5.01 ± 0.04 to 9.79 ± 0.06 and back to 5.02 ± 0.01 , being more significant as from 70% of

338 relative humidity. For relative humidity values less than 70%, the rise is weak, from 5.01 ± 0.04

339 to 5.76 ± 0.03 , indicating that the dielectric permittivity is not impacted by the amount of water

340 sorbed within the wheat gluten layer. As from 70% of relative humidity, the permittivity

341 increases significantly to higher values, illustrating that an increasing amount of water is sorbed

342 and participate in the dielectric behavior of the polymer. If figure 7 is considered, it can be

343 observed that the dielectric permittivity increases linearly as from 8% of water content (~50%
344 relative humidity). Under these 8%, all few water molecules present are directly linked to the
345 hydrophilic groups of the wheat gluten network. These water molecules are not mobile and are
346 not available for any kind of chemical reaction. Consequently, they can neither participate to
347 degradation reactions within food materials, nor to the dielectric permittivity of wheat gluten.
348 With increase in water content, water accumulates in successive layers which are more and
349 more mobile and thus available for a participation in degradation reaction in food products and
350 in the measurement of the dielectric properties. Therefore, dielectric property measurement also
351 gives a measure of the availability of water molecules in the protein network.

352

353 Figure 6: **Simulated** dielectric loss (a) and **simulated** dielectric permittivity (b) of wheat gluten
354 as a function of relative humidity (RH) at 868 MHz, at 25°C.

355

356 Figure 7: **Simulated** dielectric permittivity of wheat gluten layer as a function of water content
357 at 868 MHz, at 25°C.

358

359 **Effects of relative humidity:** Wheat gluten, in the present case, is in contact with surrounding
360 relative humidity, which increases from 20% to 95%. Phenomena taking place at these relative
361 humidity values are diverse. At low relative humidity (20%), the water content in the film is
362 3.6% dry basis (figure 3), indicating that wheat gluten is in its dry state. The small percentage
363 of water is considered to be bound water to the highest energy sorption sites, and has little
364 contribution to the dielectric properties of wheat gluten. In addition, the high cross-linking of
365 glutamine (content: 45%) is probably responsible for protein-protein interactions, not favoring
366 protein-water interactions, forming a dense network and a cohesive, unplasticized gluten film.
367 The same phenomenon on the flexibility of native wheat gluten at low relative humidity was

368 also observed [29]. When the latter increased, more water molecules are adsorbed on the surface
369 of wheat gluten and absorb through the protein layer. The sorption process increases the water
370 content in the wheat gluten layer, where 8.03% of water content on a dry basis is obtained for
371 50% and 10.2% d.b at 70% of relative humidity. At this stage, it can be stated that all the polar
372 sites are occupied by water molecules with the formation of the monolayer. When relative
373 humidity is more than 70%, additional water concentrates within the layer forming clusters
374 (accumulation of layers) which continuously increase in size with water addition. Once clusters
375 are increasing, changes such as protein conformation, internal protein mobility and mobility of
376 water molecules take place. These water molecules are then considered as free water at more
377 than 90% RH, able to move within the network, and even more under the influence of an electric
378 field, due to their polarity. As it was specified in section 3.1.2 and figure 3, different types of
379 binding between water molecules and wheat gluten are formed:

- 380 i) 20%-50%: Few bind water molecules.
- 381 ii) 50%-70%: Bind water molecules to high energy sorption sites (monolayer
382 formation).
- 383 iii) 70%-90%: Cluster formation with formation of hydrogen bonds to water molecules,
384 with increasing movement of the molecular chain.
- 385 iv) >90%: Presence of free water.

386 According to the water sorption measurements, the water content in the film at 95% of relative
387 humidity is equal to 33.6%. It was demonstrated that the glass transition temperature (T_g) was
388 related to relative humidity and temperature. Other authors state that below 22% of water
389 content, wheat gluten is considered dry in a glassy state and that the T_g is up to 110°C at 25°C
390 [17,30–32]. Increasing relative humidity up to 82.5% (water content: 20% dry basis) results in

391 a T_g around 25°C (current experiment temperature). Therefore, increasing water molecules
 392 plasticizing the polymer matrix lowers T_g of the polymer, so that the transition from glassy to
 393 rubbery state takes place at a lower temperature value. This change in the protein conformation
 394 gives freedom to mobility of macromolecular chain and to a further extent, smaller elements
 395 such as amino acids and water molecules.

396 **Effects of relative humidity on dielectric loss:** The dielectric loss is characterized by energy
 397 dispersion of the relaxation phenomena of dipoles taking place in the network, produced at
 398 microwave and radio frequencies. The dielectric loss can be modeled by equation 4,
 399 representing the different contribution phenomena. Conduction in the network is ionic based,
 400 obtained from residual free charges found in the network, such as residual salts in the present
 401 case [33].

$$\varepsilon'' = \varepsilon''_d + \frac{\sigma}{\varepsilon_0 \omega} \quad \text{Equation 4}$$

402 where ε''_d represents the loss factor due to dipolar orientation and relaxation, and $\sigma/\varepsilon_0\omega$
 403 represents the loss factor caused by ionic conductivity with σ , ε_0 and ω representing the
 404 conductivity of the material, the dielectric constant of vacuum and the angular frequency
 405 respectively.

406 It is important to specify that the relaxation phenomena are slow processes and are not produced
 407 instantaneously, and that ionic conductivity only introduces losses into the polymer when
 408 exposed to electromagnetic energy. Loss due to dipolar relaxation results from the movement
 409 and frictional motion of the constituent dipoles (dipole-dipole interactions) which is
 410 transformed into heat energy [34,35]. At low water content, mainly relaxation phenomena
 411 contribute to dielectric loss instead of ionic conduction in dry wheat gluten under the influence
 412 of the electromagnetic field. As the level of hydration increases, wheat gluten becomes

413 plasticized with more freedom for the motion of its different constituents, resulting in a rise in
414 the extent of charge movement, bringing electrical conduction within the layer [16,27]. At this
415 high hydration level, dielectric loss is mainly due to ionic conduction [36] and are facilitated
416 by free water retained by capillarity within the wheat gluten layer. Ionic conduction could hide
417 the dipolar losses effect [33]. The overall result remains that the effective dielectric loss ϵ''
418 increases with relative humidity.

419 **Effects of relative humidity on dielectric permittivity:** The charged network of wheat gluten,
420 the hydrogen bonds linking the protein chains, the dipolar interactions of amino acids confer
421 wheat gluten its dielectric permittivity under the influence of an electromagnetic field. At low
422 hydration level (20% of relative humidity), few water molecules bind to the wheat gluten
423 network. This binding is progressive up to 70% of relative humidity. At this point, the maximum
424 water content in the wheat gluten layer is 10.2% on a dry basis. The charged network and
425 hydrogen bonds of water molecules with the side chains of amino acids participate in the
426 dielectric permittivity. Increasing relative humidity (to more than 70% RH) results in a
427 considerable increase in water content within the wheat gluten layer. Between 70% and 90%
428 of relative humidity, the water content increases from 10.2% to 23.09% on a dry basis, and an
429 increase of 23.09% to 33.6% of water content for a rise in relative humidity of 90% to 95% is
430 recorded. When plasticizers such as water molecules bind to the wheat gluten, under an
431 isothermal process, the effect is the same as an increase in temperature on the molecular
432 mobility. Water, being a low molecular weight component, increases free volume and hence
433 increases backbone chain segmental mobility [30], as well as elements such as dipoles and
434 amino acids under the influence of an electromagnetic field.

435 The rise in water content has a significant impact on the permittivity of the wheat gluten layer,
436 as free water, being a dipole with a strong dipolar moment [27,37,38], having a high permittivity

437 of approximately 80 [39–42] drastically increases the effective dielectric permittivity of the
438 wheat gluten layer.

439 3.4 Sensitivity

440 A better insight of the wheat gluten response can be obtained using partial sensitivities. The
441 capacitance sensitivity has been calculated in order to be compared in an easier manner to the
442 literature. The capacitance was calculated using a resistance capacitance model and the
443 sensitivity was calculated using equation 5.

$$S = \left(\frac{C^u - C^i}{X^u - X^i} \right) \quad \text{Equation 5}$$

444 where S represents the sensitivity of wheat gluten coated IDC. C represents the capacitance
445 value. X represents the concentration of relative humidity. u represents the final values and i
446 the initial values.

447 The change in the capacitance values occurs between 20% and 95% of relative humidity. Figure
448 8 reveals four distinct regions: one between 20% and 50% of relative humidity where the
449 sensitivity is low equal to 2.14 ± 0.03 fF/%RH, the second between 50% and 70% relative
450 humidity where the sensitivity is equal to 9.65 ± 0.23 fF/%RH, the third region between 70%
451 and 90% of relative humidity with a sensitivity value of 46.84 ± 0.05 fF/%RH and finally the
452 fourth region between 90% and 95% with a much higher sensitivity value of 162.0 ± 0.6 fF/%RH.
453 The graph pattern (exponential behavior) is not common to synthetic relative humidity sensors
454 (usually having a linear behavior) found in literature [43,44]. The pattern intrinsic to wheat
455 gluten is closer to food material behavior and is in a better way adapted for the monitoring of
456 packed food products, which is advantageous over synthetic humidity sensors. For example,
457 the region above 90% RH gives a particularly high sensitivity indicating that wheat gluten can

458 be ideally used for monitoring food packages with high relative humidity products (fruits and
459 vegetables). The sensitivity can be intelligently optimized in order to adapt wheat gluten to the
460 focused application.

461 Table 2 summarizes results of sensitivity and hysteresis of a natural polymer, synthetic
462 polymers and oxide based sensors. Most of the presented materials are meant for RFID
463 applications and for humidity sensors in general, foreseen to be applied in RFID technology.
464 The results obtained in the present study are in the range of those presented in the table. The
465 sensing material of high performance giving the best sensitivity (111 pF/%RH) is Cerium (IV)
466 oxide [44], which is 10000 folds higher than the present study. The study, performed at low
467 frequency (10 kHz), may explain this high sensitivity. The other types of sensor developed are
468 porous aluminum oxide based, having sensitivities of 483 fF/%RH and 4200 fF/%RH [45,46].
469 The porous aluminum oxide layer contain nano-pores on the sensitive layer, able to absorb large
470 amounts of water, increasing considerably the permittivity, and thus the sensitivity [24].
471 Moreover, this effect is optimized with an increase in the thickness of the film, as the volume
472 of the nano-pores increased as well [45]. Materials with a lower but honorable sensitivity are
473 wheat gluten (162.0±0.6 fF/%RH) (present study), polyethylene-naphthalate and polyimide
474 foils (21 fF/%RH) [47] and polyphenylacetylene (PPA) (10 fF/%RH) [48]. With the exception
475 of wheat gluten developed in the present work which is a natural polymer, the other two are
476 synthetic polymers. The sensors with the lowest sensitivity values are polyimide [43] and
477 cellulose acetate butyrate [49], which are synthetic polymers and thermoplastic based on
478 cellulose acetate. Their sensitivity values are 4.5 fF/%RH and 1.5 fF/%RH respectively.

479
480 Figure 8: Sensitivity of wheat gluten coated IDC system as a function of relative humidity.

481 3.5 Hysteresis

482 Hysteresis is an important design parameter. It can be defined as the difference in the output
 483 signals when measured for the up-trace and down-trace of the input signal. Comparing between
 484 the increasing and decreasing permittivity values, a weak hysteresis can be noticed between the
 485 up-trace and down-trace. The maximum hysteresis equal to 7% at 90% of relative humidity was
 486 calculated using equation 6.

$$Max\ Hysteresis = \frac{\max|C_{dec} - C_{inc}|}{C_{max} - C_{min}} \times 100\% \quad \text{Equation 6}$$

487 where C_{dec} represents the decreasing capacitance value, C_{inc} the increasing capacitance value,
 488 C_{max} and C_{min} the maximum and minimum capacitance values.

489 With increasing water content, modification in the protein film conformation occurs,
 490 particularly unfolding and exposure of polar residues, favoring water uptake within the layer,
 491 and resulting in the swelling of the layer. Upon desorption (decrease in water content), the slow
 492 shrinkage of the wheat gluten layer resulted in a hysteresis due to conformational changes
 493 involving structural relaxation (coming from clusters of absorbed water), noticeable on the
 494 dielectric permittivity and loss of wheat gluten (figure 6). This phenomenon is also observed
 495 on various polymers [49,50] and humidity sensors [36,45]. The swelling/shrinkage process of
 496 the wheat gluten matrix is often time dependant. At the end of the desorption process, the layer
 497 is brought back to its original state, where it is considered that no free water is present within
 498 the layer, but only bound water, with the same structure as at 20% RH, indicating its
 499 reversibility. Table 2 gives an overview of the hysteresis for the different materials, where only
 500 1% of maximum hysteresis is obtained for cerium(IV) oxide at 45% of relative humidity. The
 501 hysteresis obtained in the present study is in the range of the other materials, being equal to 7%

502 for wheat gluten and 16% for anodic aluminum oxide [46], 20% for cellulose acetate butyrate
503 [49], 10% for polyimide films [43] and a maximum of 30% for anodic aluminium oxide [45].

504

505 Table 2: Humidity sensors characteristics found in literature and in this study.

506

507 4 Conclusion

508 Wheat gluten protein has been investigated for relative humidity monitoring. Interdigital
509 capacitors have been used for performing electrical measurements, and the dielectric loss and
510 permittivity of wheat gluten were determined by retro-simulation at 868 MHz. The electrical
511 and dielectric characterization of the wheat gluten layer showed that the natural polymer is
512 hydrophilic with significant changes at high relative humidity values (>70%), rather than at
513 lower relative humidity values. The permittivity increased from 5.01 ± 0.04 to 9.79 ± 0.06 and the
514 dielectric loss from 0.39 ± 0.01 to 1.48 ± 0.02 when relative humidity increased from 20% to 95%.
515 This rise, mainly due to water molecules, was confirmed by the net mass intake of water
516 reaching up to 33.6% d.b in the wheat gluten film. The results indicated a good sensitivity of
517 wheat gluten at high relative humidity values, ideal for foreseen applications related to the
518 monitoring of packed food products. The different phases of water interaction between water
519 dipoles and the wheat gluten molecular structure have been presented, at low, medium and high
520 hydration level, with the material response depending mainly on the percentage of linked and
521 free water present.

522 To a further extent, optimization of the sensor could be performed in order to adapt its
523 sensitivity to targeted applications. Plasticizers, such as glycerol, may be used as additives to
524 increase the mobility of the elements in the network and be used for food products having a
525 lower water activity. Another modification that can be considered is the manufacture of a

526 porous wheat gluten layer, able to absorb water molecules through its nano-pores, increasing
527 even more the sensitivity of the layer. According to the generally high accuracy of results
528 obtained, wheat gluten sensors could be used in cost-effective passive UHF RFID tags, with
529 humidity monitoring capabilities.

530

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537 smooth progress of the study.

538 7 Abbreviations

539 FEM, finite element method; IDC, interdigital capacitor; RC, resistance capacitance; RH,
540 relative humidity; RFID, radio frequency identification; WG, wheat gluten; d.b, dry basis; UHF,
541 ultra high frequency; DVS, dynamic vapor sorption; **VNA, vector network analyzer.**

542

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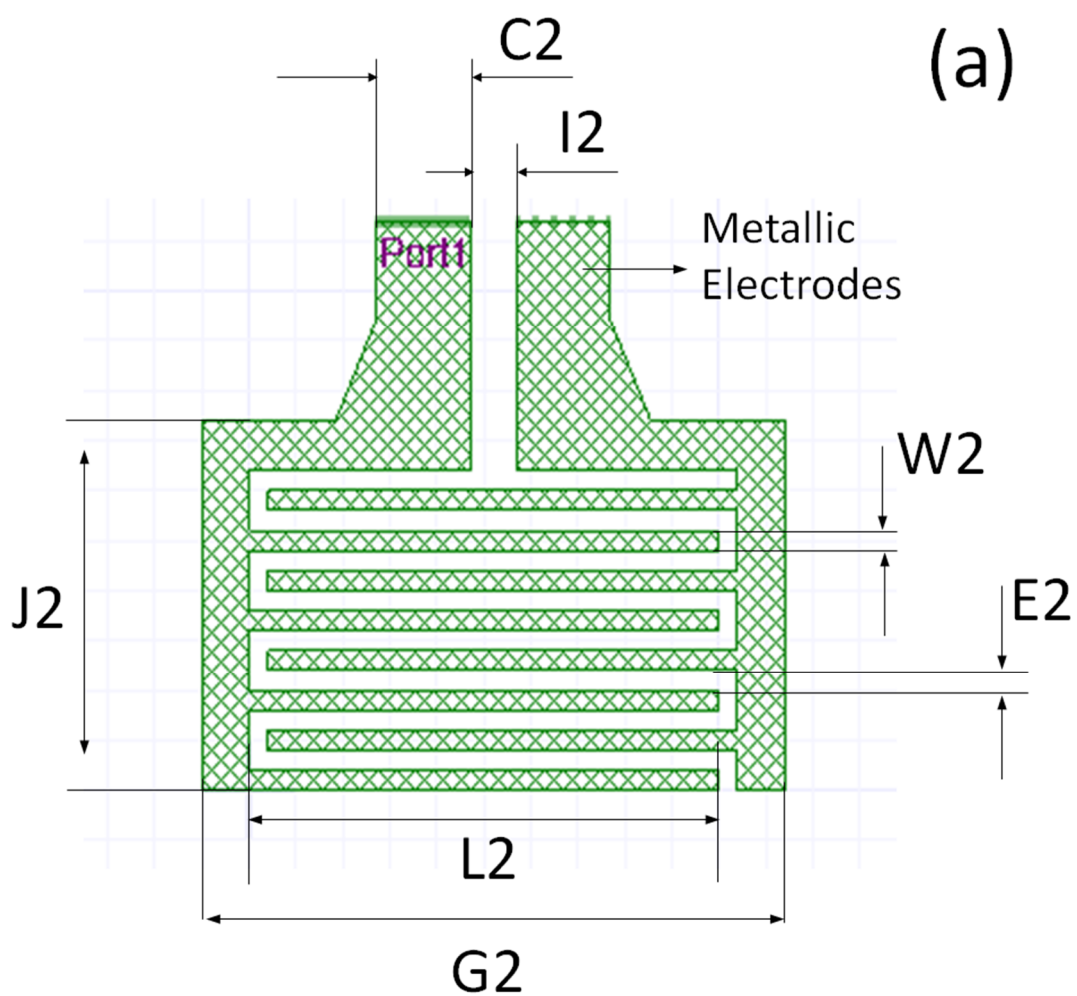
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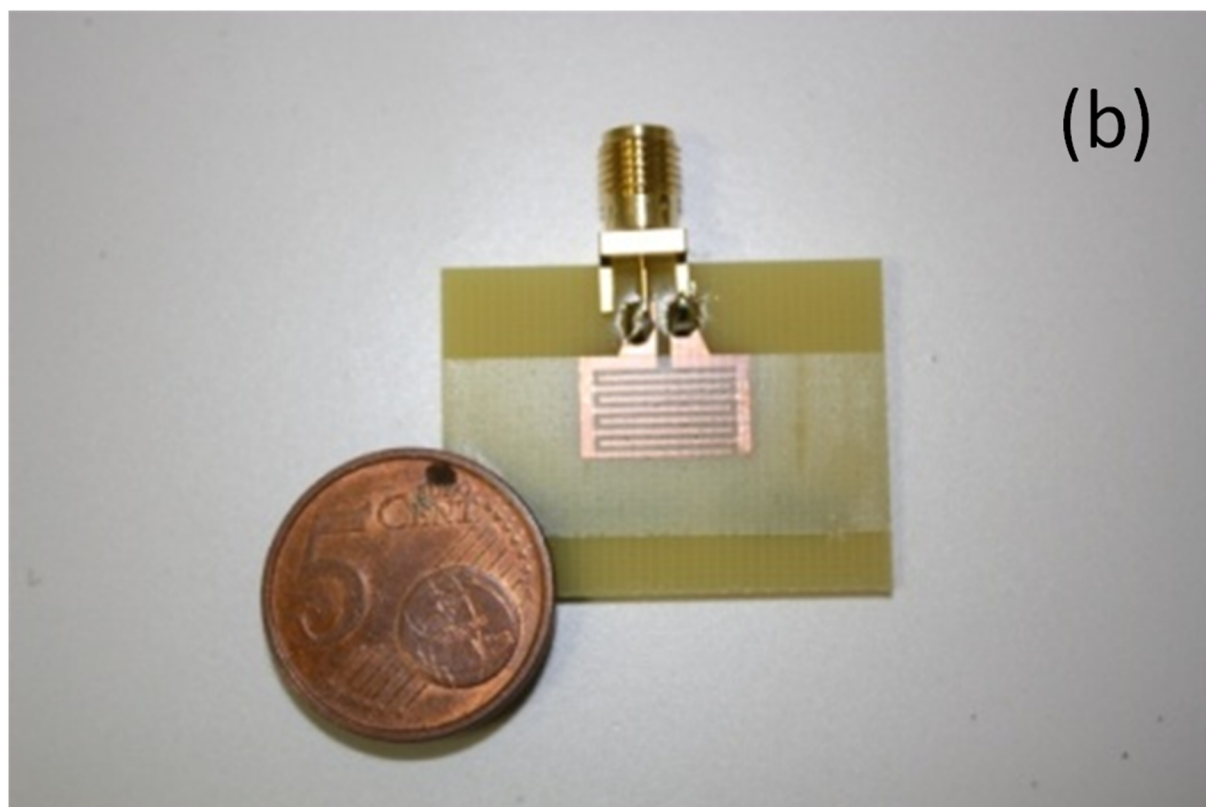
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Captions for figures



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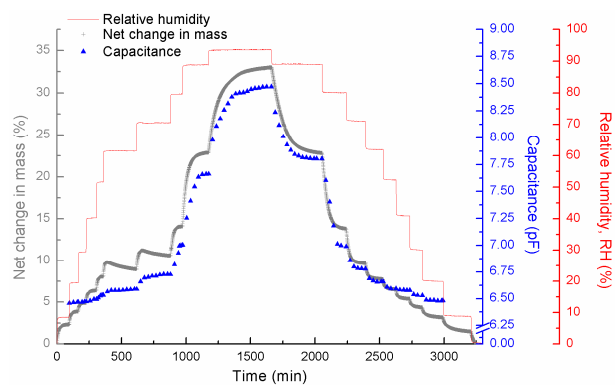
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728 Figure 1: Designed interdigital capacitor (a), manufactured interdigital capacitor system
 729 casted with wheat gluten having a capacitive behavior up to 1000 MHz (b).

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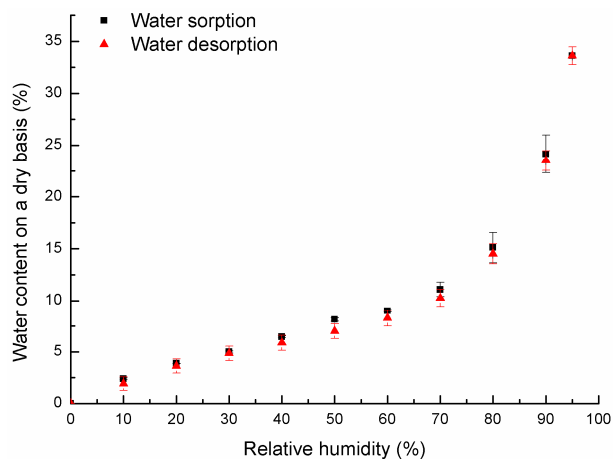


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733 Figure 2 : Net change in mass (+) and capacitance (▲) of wheat gluten layer as a function of
 734 relative humidity (—) and time.

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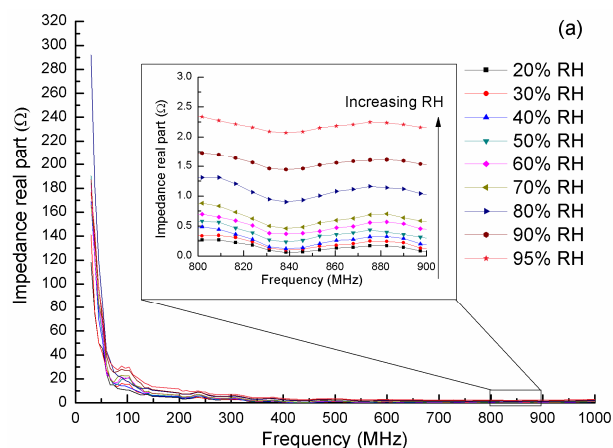


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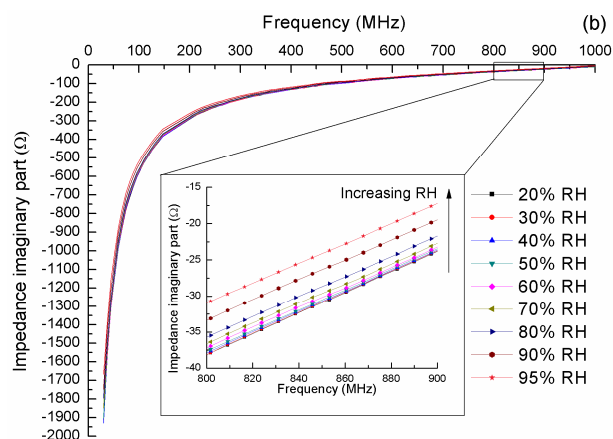
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738 Figure 3: Absorption and desorption isotherms of wheat gluten conditioned at different
739 relative humidity values.

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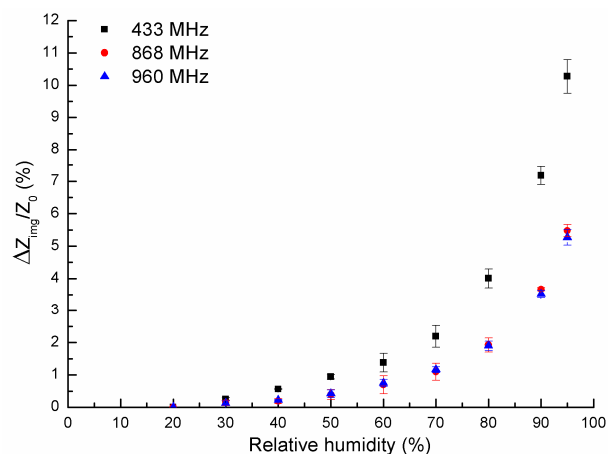
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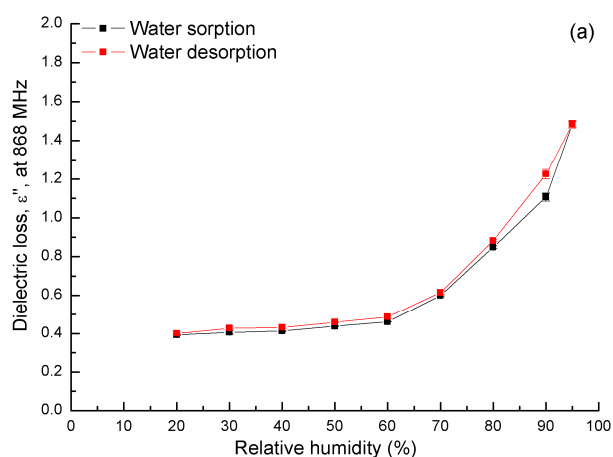
744 Figure 4: Impedance real (a) and imaginary (b) component as a function of frequency from
745 20% to 95% of relative humidity (RH), at 25°C.



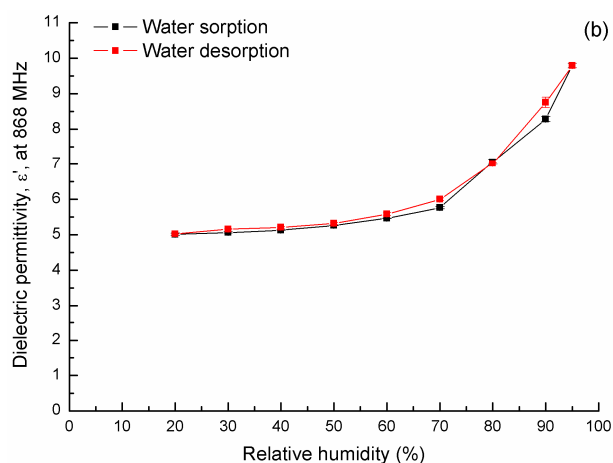
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747 Figure 5: Relative variation of the impedance imaginary component with increase in relative
 748 humidity, at 433 MHz, 868 MHz and 960 MHz.

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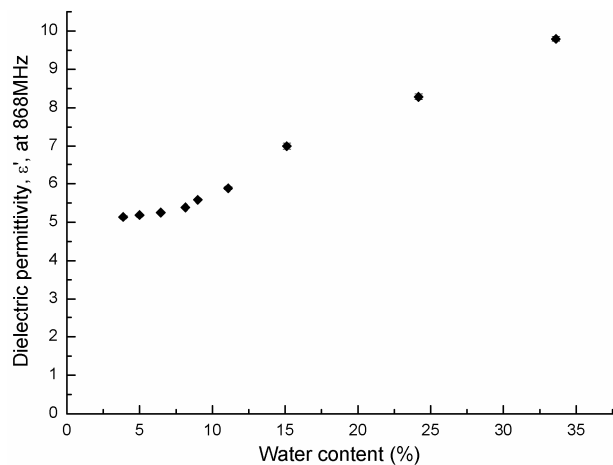


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753 Figure 6: **Simulated** dielectric loss (a) and **simulated** dielectric permittivity (b) of wheat gluten
 754 as a function of relative humidity (RH) at 868 MHz, at 25°C.

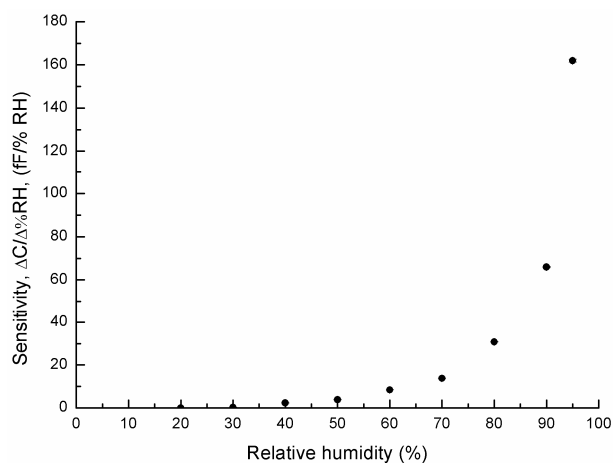
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757 Figure 7: **Simulated** dielectric permittivity of wheat gluten layer as a function of water content
 758 at 868 MHz, at 25°C.

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762 Figure 8: Sensitivity of wheat gluten coated IDC system as a function of relative humidity.

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770 Table 3: Comparison of experimental and simulated electrical properties of uncoated IDC
771 systems.

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	Impedance real component (Ω)	Impedance imaginary component (Ω)	Capacitance (pF)
Measured values	1.54 \pm 0.05	-28.29 \pm 0.93	6.41 \pm 0.04
Simulated values	1.46 \pm 0.12	-28.20 \pm 0.22	6.45 \pm 0.02

773

774 Table 2: Humidity sensors characteristics found in literature and in this study.

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Material	Type	Max. Sensitivity	Max. Hysteresis	Application	References
Wheat gluten (film)	Natural polymer	162.0 \pm 0.6 fF/%RH between 90% and 95% RH	7% at 90% RH	Agrifood sector- Passive RFID	Present study
Anodic aluminum oxide	Oxide	483 fF/%RH	30% at 92% RH	Humidity sensors	[45]
Polyethylene-naphthalate and polyimide foils	Synthetic polymer	21 fF/%RH	-	Intelligent RFID	[47]
Polyimide	Synthetic polymer	4.5 fF/%RH	10% at 50% RH	Humidity sensor for RFID for monitoring environmental humidity	[43]
Cellulose acetate butyrate	Synthetic polymer	1.5 \pm 0.03 fF/%RH	20% at 20% RH and 30% RH	Low cost sensor arrays and disposable sensing platforms	[49]

Porous aluminum oxide	Oxide	312.5 fF/%RH	-	-	[24]
Polyphenylacetylene (PPA)	Synthetic polymer	10 fF/%RH	-	-	[48]
Anodic Aluminum oxide	Oxide	4200 fF/%RH	16.5% at 70% RH	Humidity sensors	[46]
Cerium(IV) oxide	Oxide	111 pF/%RH	1% at 45%RH	Humidity sensors	[44]

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